

Development of Calibration-Free Autonomous Chemical Sensors for Ocean Biogeochemical Measurements

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LONG-TERM GOALS

The long term goal of the project is to develop autonomous chemical sensors for oceanographic applications. The autonomous sensors will be used on moorings, drifters and other unmanned platforms to study ocean biogeochemical processes. The results obtained from the autonomous sensors will help quantify ocean biogeochemical fluxes and will be used to further develop coupled physical-biogeochemical models of the surface ocean. Improvements in current models will allow more accurate predictions of the effects of climate change and other anthropogenic impacts on ocean biogeochemical cycles.

OBJECTIVES

The primary objective is to determine if other chemical sensors can be developed based on the calibration-free design discovered by the PI during the development of a $p\text{CO}_2$ sensor (DeGrandpre et al. 1995, 1999). If the design proves applicable to other analytes, it will be possible to develop autonomous sensors for these analytes that have an identical sensor-to-sensor response with excellent long-term stability, potentially eliminating the need for periodic calibrations.

APPROACH

The analytes total ammonia, silicate, and calcium will be initially investigated. The method requires that an indicator chemistry be used that has two different colored forms in the presence of the analyte as described for the $p\text{CO}_2$ sensor in DeGrandpre et al. (1999). The absorbances of the complexed and uncomplexed forms of the colored reagent (indicator) are combined to obtain a response that is only dependent upon the indicator equilibrium composition. Different reversible reagent chemistries that have been reported in the literature will be investigated. We have proposed to utilize an acid-base indicator for detection of total ammonia. We found a possible alternative to the standard molybdenum blue reaction for silicate, which utilizes the first step of the standard method, formation of a reversible molybdosilicic acid complex. Others have improved the sensitivity by formation of a reversible ion associate with the complex (Saurina and Hernandez-Cassou 1995). We plan to design the Ca sensor after that reported by Chau and Porter (1990) which utilized calcichrome and an ion exchange membrane. Calcichrome has different absorption spectra in the calcium-complex and uncomplexed forms making it an ideal indicator for testing the calibration-free methodology.

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WORK COMPLETED

We have begun a thorough literature search to determine if the above reagents are the best possible reagents for each analyte. Equipment has been purchased including a new research grade UV-VIS spectrophotometer that was included as part of the grant. A graduate student working on the project has designed a membrane gas exchange cell for measurement of total ammonia. Plastic fabrication components have been purchased for the flow cell. We are also evaluating new optical design for the sensing systems including a completely integrated fiber optic filter spectrometer and other miniature spectrographs. I am also currently recruiting additional graduate students to work on the project.

RESULTS

Because we are in the early stages of the funding there are no results to date.

IMPACT/APPLICATION

There is a great demand for low maintenance chemical analyzers and sensors that provide high quality data. If the technology used for the PI's $p\text{CO}_2$ sensor proves applicable to other analytes, new sensors would become available for a wide-array of applications. Although our interest lies in the area of ocean biogeochemistry, autonomous chemical sensors would also find wide use in industrial, biomedical, environmental, and defense-related applications.

TRANSITIONS

Our work has been published in the peer-reviewed literature and others may be pursuing development of their own calibration-free designs based on these papers. The $p\text{CO}_2$ sensors are now commercially available (see sunburstsensors.com) and we plan to continue to spin-off new sensor technology to the private sector to make the sensors available to researchers, government agencies, etc.

RELATED PROJECTS

At this point there are no related projects being pursued.

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PUBLICATIONS

None